

LIGHT OLEFIN PRODUCTION, SKELETAL OLEFIN ISOMERIZATION AND ETHERIFICATION FOR OXYGENATED FUEL PRODUCTION

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ARCO's newly developed SUPERFLEXSM process offers opportunities to product high yields of light olefins from a variety of readily available refinery and petrochemical feedstocks. The process is unique in that it employs a catalytic reactor system which is lower in capital and operating costs than conventional steam cracking reactors. The SUPERFLEX process is also more selective for production of propylene and butylenes (including isobutylene) than conventional steam cracking operations. The C₄ product stream from the SUPERFLEX process contains about 20 to 30 percent isobutylene. The SUPERFLEX C₄ product is, therefore, an excellent feedstock for producing MTBE via reaction of the contained isobutylene with methanol. After MTBE production, the isobutylene depleted C₄ stream may be recycled to the SUPERFLEX process to produce additional isobutylene and propylene. This paper will focus on the chemistry and mechanism of catalytic cracking and skeletal olefin isomerization. In addition, there will be some discussion on catalyst activation, life and characterization.

Light Olefin Sources

There are several commercial routes to light olefins. Traditional routes are steam cracking(1), fluid catalytic cracking(2), dehydrogenation(3) and metathesis(4). Recently ARCO Chemical company has developed a new technology known as SUPERFLEXSM which catalytically cracks higher paraffins and olefins in high selectivity to propylene and isobutylene(5). Unlike steam cracking, the propylene to ethylene ratio is high. In addition the butylenes and pentenes are isomerized to their thermodynamic distribution. This technology offers an alternate, low capital route to light olefins. It may be readily integrated into an olefins plant or refinery. Its scale-up is simplified by its analogy to the FCC process. Analogies in operating conditions are given in Table I.

SuperflexSM Technology

The SUPERFLEXSM technology has been demonstrated with olefin plant and refinery streams and with pure components such as isobutylene, butene-1, isopentane, n-pentane, cyclopentane and octane. An integrated pilot unit designed to simulate commercial operation has operated for two years. During this operation catalyst life was confirmed under simulated commercial operation, including recycle. In addition the catalyst was produced on commercial scale. Catalytic activity is sufficient to approach olefin equilibrium in 5 to 15 seconds. Selectivity to aromatics and paraffins is minimal. Catalyst attrition is low with less than 15 wt % loss on the 5 to 15 hour portion of the ASTM D-32.02 TG 06 Jet Attrition Test. Catalyst hydrothermal stability is good with less than 1% activity loss per day. The active catalyst component is a modified ZSM-5. It is formulated into a fluidizable catalyst by combining it with a matrix of silica and kaolin and spray drying. The catalyst working environment is given in Figure 1.

Catalyst Evaluation

Numerous zeolites were synthesized, characterized and evaluated in catalytic cracking reactions to light olefins. H-ZSM-5 was found to be most active and selective. Others of noteworthy activity are listed in Table II. The Si/Al ratio of H-ZSM-5 was varied from 20 to 100. A ratio of approximately 40 was found to be optimal. An inexpensive, non-template H-ZSM-5 performed similar to that of a template one.

Catalyst evaluations were run with 60 to 100 mesh fixed beds consisting of active catalyst diluted in alpha alumina to adjust conversion to reasonable levels. The beds were held in quartz reactors of 6.5 mm i.d. containing a 2 mm o.d. thermowell. Bed lengths were typically 4 cm and bed volumes 1.4 ml. Results were obtained at 550 to 600 °C and 1 atm total pressure. The WHSVs are with respect to the active component of the bed (not including diluent alumina).

Hydrothermal Stability

Resistance to steam deactivation is important for catalyst performance and life since commercial catalytic cracking units operate in the presence of steam and steam is generated in-situ during coke burn-off. Hydrothermal treatment of a catalyst containing H-ZSM-5 with no modifiers caused a two-fold decrease in catalyst activity. Numerous modifiers were evaluated of which phosphorous was most successful. Hydrothermal treatment of a catalyst containing P,H-ZSM-5 increased 2-butene cracking activity fourfold. Deactivation was not evident with subsequent hydrothermal treatments and time on stream. In fact, to maintain high activity continuous or intermittent exposure to steam was necessary. Initial activation of fresh catalyst required more severe steaming at 1100 °F and 1 to 2 atm for 1 to 2 days. Steam pressures of 0.02 to 1 atm were adequate for activity maintenance. A weight loading study indicated the optimal phosphorous loading was close to 1 wt %. Phosphorous was most readily added to the H-ZSM-5 or matrix containing H-ZSM-5 by incipient wetness impregnation with phosphoric acid followed by drying at 120 °C and calcining at 600 °C for 2 hrs. The hydrothermal activation studies are given in Table III and the effect of steam in the feed is given in Table IV.

Characterization of H-ZSM-5 and P,H-ZSM-5

^{27}Al and ^{29}Si MAS NMR of H-ZSM-5 indicated that silicon was in a highly silicious environment typical of H-ZSM-5 for both the fresh and steamed samples. Steaming resulted in fine structure typical of dealumination(6). Aluminum was tetrahedrally coordinated within the zeolitic framework. With steaming, dealumination was evident. There was a decrease in signal intensity for zeolitic aluminum. Non-framework octahedral aluminum became evident(7).

^{27}Al , ^{31}P and ^{29}Si MAS NMR of P,H-ZSM-5 indicated phosphorous was bound to the framework and dealumination had occurred with phosphorous incorporation. With severe steaming phosphorous remained bound to the framework and further dealumination was evident. Silicon remained in a highly silicious environment typical of H-ZSM-5 with phosphorous addition and steaming. Once steamed and equilibrated no further dealumination was evident.

A mechanism for phosphorous bonding to the zeolite framework is given in Figure 2. Phosphorous converts strong Bronsted acid sites into weak ones. On doing so, the pore radius decreases and the geometry at the acid site is altered. Further reaction results in dealumination with AlPO_4 formation.

A constraint index experiment on P,H-ZSM-5 suggested phosphorous was blocking the channels and that catalysis was occurring at the pore mouth and external surface. Using literature procedures (8) the P,H-ZSM-5 gave a constraint index of < 1 whereas, the unmodified H-ZSM-5 gave a constraint index of 10.8. The low constraint index for the phosphorous modified H-ZSM-5 indicated the zeolite no longer discriminated between linear and branched hydrocarbon feed. This was largely attributed to the fact that nearly all reactivity occurred external to the channels. In a separate study a phosphorous modified H-ZSM-5 was analyzed by high resolution electron microscopy (9). In this study it was likewise concluded that phosphorous was blocking the zeolite channels.

Mechanistic Studies

Compared to steam cracking and FCC technology, the SUPERFLEXSM process is best conducted at higher space velocities and temperatures ranging from 550 to 625 °C. Best results are obtained under diffusional limiting conditions under which the majority of the chemistry occurs at the pore mouth where super acid sites are available. For butene conversion the reaction is bimolecular. Two molecules of butene react to give octene which subsequently disproportionates to olefins, alkanes and aromatics. See Figure 3. A second order rate constant of $1.1 \times 10^7 \text{ cm}^3/\text{mole sec}$ has been experimentally determined. Little or no diffusion into the pore occurs since the rate of diffusion is much slower, less than or equal to $1 \times 10^{-8} \text{ cm}^2/\text{sec}$. (10).

n-Butene Skeletal Isomerization

A major objective was to integrate skeletal isomerization with SUPERFLEXSM to make more isobutylene and isoamylene for MTBE and TAME production. By adjusting reaction conditions skeletal isomerization could be conducted successfully over the SUPERFLEXSM catalyst. Higher temperatures, 625-650 °C vs. 550-625 °C, favored isomerization over cracking. This is largely due to the fact that cracking is a bimolecular process requiring longer surface residence time. Whereas the skeletal isomerization is a

uni-molecular process. By a similar argument, increased pressure favored cracking. Due to the fact that steam generates more Bronsted acid sites, under these conditions cracking was favored. Whereas, with no steam, Lewis acid sites predominated and skeletal isomerization was favored. Iso-olefin selectivities increased with gas velocity due to increased mass transfer rates.

The SUPERFLEXSM catalyst ran in a pilot fluid bed unit and gave 15% isobutylene yield under optimal isomerization conditions while meeting productivity, life, attrition and cost targets. Results from the lab and pilot unit are given in Table V. In addition, a catalyst consisting of Mg-APSO-31 was found to be effective for skeletal isomerization (11). It was more selective than the SUPERFLEXSM catalyst due to lower acidity yet was lower in activity and more expensive. See Table V for results.

Etherification

A process scheme for converting the iso-olefins produced from an isomerization unit to ethers was proposed and patented (12). The process scheme could potentially utilize the approximately 350,000 BBL/day of C₅⁼ olefins produced at U.S. refineries. The combined mole fraction of 2-methyl-2-butene and 2-methyl-1-butene at equilibrium exceeds 0.80 at 300 °F. These olefins may be converted to TAA and/or TAME.

Conclusions

A new technology for producing light olefins in high yields has been developed which uses a phosphorous modified H-ZSM-5. The catalyst has been extensively evaluated in a pilot unit and found to withstand hydrothermal and attrition testing. By modifying the reaction conditions skeletal olefin isomerization may be conducted with the same catalyst. Finally, an iso-olefin etherification step may be carried out for oxygenated fuel production.

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TABLE I
SUPERFLEX PROCESS
COMPARISON WITH FLUID CATALYTIC CRACKING

	SUPERFLEX DESIGN	FCC
Coke Yield, Wt %	< 1	3 to 7
Riser Temp., °C	550 to 650	500 to 550
Regen Temp., °C	625 to 725	675 to 775
Feed	C ₄ to C ₁₀	Gas Oil (C ₁₂ **)
Cat/Oil, Wt	12 to 25	5 to 8
Catalyst Make-Up Rate, %/day	1.0 to 2.5	1.0 to 2.0

TABLE II
2-BUTENE CONVERSION

Catalyst	Temp °C	WHSV hr ⁻¹	% C ₄ ⁺ Conv	% Selectivity					
				C ₃ ⁺	C ₂ ⁺	C1-4	C5,6	Coke	BD
H-ZSM-5 (HCl Prep)	550	833	68.9	50.6	11.2	10.9	27.0	0.2	0.2
H-ZSM-5 (NH ₄ Cl Prep)	550	833	68.9	45.8	7.9	9.7	35.9	0.6	0.2
H-ZSM-11	550	833	30.8	36.4	1.1	6.1	56.5	0.01	0.2
Beta	600	550	56.4	20.8	2.5	11.8	64.7	0.3	0.2
Zeolite Y	600	275	58.4	31.7	3.8	20.2	41.6	2.6	0.1
Mordenite	600	275	54.2	43.3	9.4	21.6	22.9	2.6	0.3
USY	550	124	64.9	28.1	3.5	38.9	29.5	2.8	0.09
H-ZSM-34	550	55	58.0	42.0	15.0	16.5	16.1	10.1	0.2
Omega	600	55	37.1	43.7	5.7	16.0	34.1	0.4	0.6
Matrix (Aluminosilicate)	600	6.9	9.4	23.7	4.1	20.6	27.7	0.9	23.9
α-Al ₂ O ₃	600	14	5.6	5.8	0.8	82.9	9.1	1.5	0.7

TABLE III

2 - BUTENE CONVERSION

EFFECT OF PHOSPHORUS AND STEAM ON H-ZSM-5

	1% P,H-ZSM-5, Prior to Hydrothermal Activation	1% P,H-ZSM-5, After Hydrothermal Activation	H-ZSM-5 Prior to Hydrothermal Activation	H-ZSM-5 After Hydrothermal Activation
Temp., °C	600	600	600	600
WHSV, HR ⁻¹	31	125	62.5	31
% C ₄ ^a Conv.	60	65	57	59
% Sel to:				
CH ₄	0.21	0.11	0.91	1.30
C ₂	0.12	0.09	0.19	0.31
C ₃ ^a	11.20	8.70	14.20	18.00
C ₃	1.10	1.40	1.60	1.80
C ₅ ^a	49.00	49.90	52.00	55.70
Isobutane	2.00	1.80	3.30	3.30
N-Butane	6.40	5.80	5.10	4.50
Butadiene	0.33	0.26	0.27	0.31
C ₅	17.40	18.10	14.60	9.40
C ₆	12.10	23.80	7.90	5.40
Coke	0.20	0.06	0.11	0.44

TABLE IV

ONCE-THROUGH LAB RUNS OF 2-BUTENE OVER COMMERCIALY
VIABLE SUPERFLEX CATALYST AT 600 °C (1110 °F)

	A	B	C	D	E	F	G
Catalyst History	Fresh	Fresh	Used 12 Days in Pilot Unit	As In C	As In C	As In C	As In C
Steam	None	Before Run 550°C, 2 atm 24 Hrs	In Regenerator 620°C, 0.2 atm, 5 Cycles/Hr	As In C, Then 2 Dry Cycles	As In D, Then 500°C, 0.5 atm, 2 Hrs	As In D, Then 600°C, 0.03 atm, 20 Sec	As In D, Then 0.1 atm in Butene and Regeneration
WHSV	65	93	65	65	130	65	70
% Butene Conversion	25	60	75	60	65	71	64
% Selectivity To:							
CH ₄	0.2	0.2	0.2	0.2	0.1	0.1	0.2
C ₂ H ₆	8	16	20	13	12	14	12
C ₃ H ₆	0.1	0.2	0.3	0.7	0.1	0.2	0.1
C ₃ H ₈	41	55	53	57	53	53	59
C ₄ H ₆	0.2	1.9	3.1	1.4	2.6	2.4	1.9
C ₄ H ₈	0.8	0.2	0.4	0.2	0.1	0.2	0.2
C ₄ H ₁₀	16	8.7	8.1	8.7	8.8	8.8	8.2
C ₅	30	11	7	14	14	12	13
C ₆	8	7	7	5	8	8	5
COKE	1.7	0.2	0.4	0.6	0.2	0.1	0.1

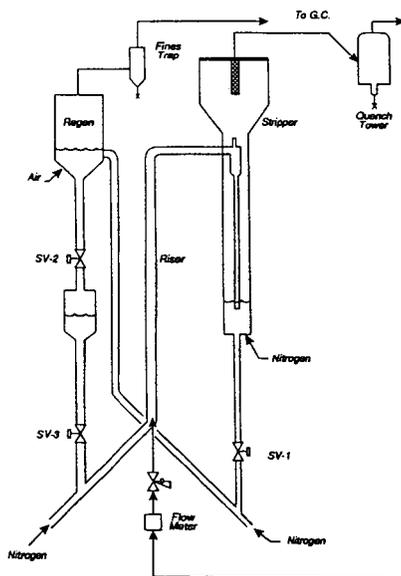
TABLE V

n-C₄= SKELETAL ISOMERIZATION

	<u>SUPERFLEX Catalyst</u>		<u>Mg-APSO-31</u>
	<u>PILOT</u>	<u>LAB</u>	<u>LAB</u>
λ YIELD %	15	19	30
λ SELECTIVITY %	25	47	80
<i>n</i> -C ₄ = CONVERSION %	60	41	38
TEMPERATURE, °C	650	625	575
WHSV, hr ⁻¹	250	296	46
LIFE	GOOD	---	TO BE DETERMINED
FLUIDITY	GOOD	---	ACTIVITY TOO LOW
ATTRITION RESISTANCE	5-7%		PROBABLY GOOD

FIGURE 1

CATALYST WORKING ENVIRONMENT



	<u>Reactor</u>	<u>Stripper</u>	<u>Regenerator</u>
Temp, °C	550 - 650	550 - 650	550 - 650
Residence Time	2 to 6 secs	4 to 5 min	4 to 6 min
% Steam	Negl.	25 to 50	5 to 20

FIGURE 2

**Mechanism for Phosphorous Bonding
to the Zeolite Framework**

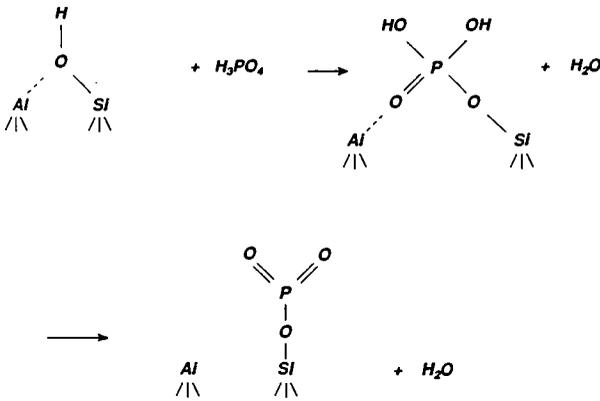


FIGURE 3

MECHANISM

